

# **Emerging Petroleum-Oriented Nanotechnologies for Reservoir Engineering**

**Igor N. Evdokimov, Nikolaj Yu. Eliseev, Aleksandr P. Losev, and  
Mikhail A. Novikov,**

Gubkin Russian State University of Oil and Gas

## **Abstract**

The paper describes experimental/analytical research aimed at modification of petroleum technologies to “nanotechnologies” by accounting for molecular processes in nanocolloids of native petroleum fluids.

Our results show that in course of traditional technological operations, macroscopic properties of petroleum media (viscosity, density, pour point, etc.) may exhibit abrupt changes caused by currently uncontrolled microscopic phase transitions in nanocolloids. In particular, our experiments provided phase diagrams of petroleum nanocolloids, which show critical parameters, highly unfavorable for industrial processing of petroleum. E.g., petroleum fluids may practically solidify at RT after a short-time residence at the temperature-defined phase boundary of ca. 28-35°C; native crudes of diverse origin exhibit sharp viscosity/density peaking at several composition-defined phase boundaries which are relevant to compatibility problems. Contrary to widespread assumptions, the current properties of petroleum nanocolloids (and, hence, the current properties of petroleum fluids) are not defined solely by current technological parameters. Of equal/decisive importance are the details of a preceding history of reservoir development.

We conclude that proper recovery “nanotechnologies” should be designed and performed with an understanding of importance of the complex nanophase diagrams of petroleum fluids. Such technology should include specifically designed processes

(employ specifically selected parameters) to purposely avoid/instigate particular phase transformations in petroleum nanocolloids in order to improve (or, at least, not to ruin) the practically important bulk properties of petroleum. With respect to immediate practical applications, it should be emphasized that the discussed phase diagrams contain only “the most obvious” nanophase boundaries, reflect our *current knowledge* of structural transformations in petroleum and should be subjected to further investigation.

## **Introduction**

Nanotechnology has been making its presence felt in the industry for some time, and many applications are already standard in petroleum refining. E.g., nanostructured zeolites are now used to extract up to 40% more gasoline than the catalysts they replaced.<sup>1,2</sup> The most obvious application of nanotechnology for upstream operations is development of better materials.<sup>3,4</sup> The oil industry needs strong, stable materials in virtually all of its processes. By building up such substances on a nanoscale, it could produce equipment that is lighter, more resistant, and stronger. Nanotechnology could also help develop new metering techniques with tiny sensors to provide improved information about the reservoir.<sup>3,4</sup> Other emerging applications of nanotechnology in oil reservoir engineering are in the sector of developing new types of “smart fluids” for improved/enhanced oil recovery, drilling, etc.<sup>4-7</sup> Among these are new nanoformulations of surfactants/polymers, microemulsions, colloidal dispersion gels (CDG), biliquid foams (aphrons). More recent developments deal with so-called “nanofluids”.<sup>6,7</sup> These are designed by introducing small volumetric fractions of nanosized solid particles to a liquid phase in order to enhance or improve some of the fluid properties. Nanofluids can be designed to be compatible with reservoir fluids/rocks and be environmentally friendly. Some newly developed nanofluids have shown extremely improved properties in such applications as drag reduction, binders for sand consolidation, gels, products for wettability alteration, and anticorrosive coatings.<sup>6,7</sup> Presently, the term “nanofluid” is used mainly to define suspensions of *solid* nanoparticles, though there is noticeable tendency to extend it to nanoparticles of any nature.<sup>8</sup> In the following this term will be used in the latter, general meaning.

In the present publication we will discuss a lesser investigated subject of upstream nanotechnologies for petroleum fluids proper. The discussion is based on our original

experimental studies and on other published experimental data. In support, we analyze available databases of the properties of world (dead) crudes. The main conclusion is that native crude oils may be classified as “association nanofluids”. Hence, all conventional/emerging technologies for reservoir engineering should be optimized/designed with an account for (still under-investigated) complex phase diagrams of intrinsic nanocolloids, primarily those formed by asphaltenes. At the least, this would help to preserve a delicate inner structure of native crudes (the approach which may be regarded as “petroleum nanoecology”).

The discussion begins with necessary descriptions of some concepts in “nanotechnologies” and “petroleum colloids”, which are frequently misinterpreted or misused.

### **What is nanotechnology? Sources of confusion about nanotechnology.**

Some persistent “nanomyths” apparently became widespread in 1966, when Isaac Asimov’s science fiction novel, “Fantastic Voyage” was made into a movie featuring adventures of the crew of a miniaturized submarine which is injected into the blood stream of a defecting scientist in order to melt an inoperable blood clot in his brain. Moreover, in 1986, Eric Drexler publishes a book<sup>9</sup> with a scientist’s idea of nanotechnology using programmed molecular sized robots called “*nanobots*” - machines that could assemble individual atoms and molecules into required structures. Fig. 1 shows an artist’s impression of nanobot (image from [http://www.thelensflare.com/gallery/p\\_nanobot\\_223.php](http://www.thelensflare.com/gallery/p_nanobot_223.php)).

**Fig. 1. Mechanical nanorobot for molecular *forced assembly*.**



In our opinion, nanotechnologies for petroleum industry have little to do with building nanobots, though a popular website **Wired.com** quotes one report that says tiny nanorobots will "patrol the pores of an oil or gas reservoir, monitor how hydrocarbons are flowing, decide how to maximize recovery, and dictate which other

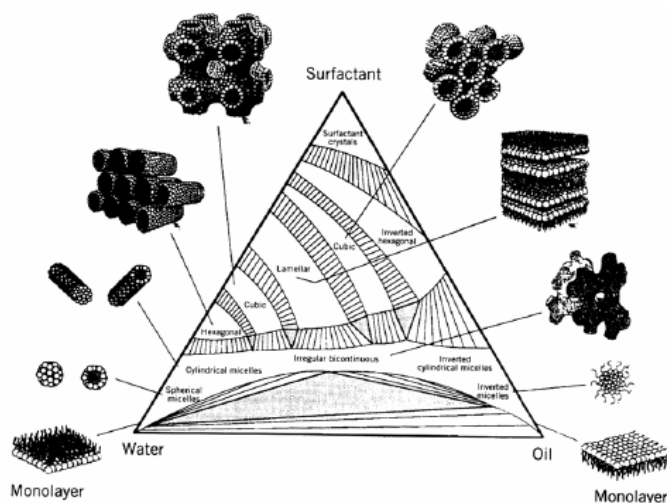
robots in the wells and zones should produce at that moment and which should inject water." Moreover, a concept of nanorobots has been a subject of some recent presentations at petroleum-oriented conferences.<sup>10,11</sup>

Currently, there are no universally accepted "precise" definitions which would allow distinguishing between "true" nanotechnologies and other domains of atomic and molecular science/engineering. The fairly representative definitions are:<sup>12</sup> "*Nanoscience* is the study of phenomena and manipulation of materials at atomic, molecular and macromolecular scales, where properties differ significantly from those at a larger scale." "*Nanotechnologies* are the design, characterization, production and application of structures, devices and systems by controlling shape and size at nanometer scale."

Note that these definitions do not refer to any specific methods/devices like nanobots. The reason is that, in fact, there are two fairly distinct branches of nanotechnology. More commonly, the term "nanotechnology" is used interchangeably with "molecular nanotechnology" (MNT), which exploits the concept of mechanosynthesis based on positionally-controlled molecular manipulation (*forced assembly*), guided by machine systems - scanning probe devices (STM, AFM) or Drexler's nanobots. As indicated, we do not expect that in the foreseeable future this type of nanotechnology will be of any importance for upstream operations.

The other branch of nanotechnology evolved as supramolecular chemistry with a fundamental concept of molecular *self-assembly* without guidance or management from an outside source. In self-assembly all final nanostructures are "encoded" in the shapes and properties of the molecules that are employed. The particular desired structures of suspended supramolecular nanoparticles may be realised by subtle changes of macroscopic system parameters, e.g. system's composition, as illustrated in the phase diagram of Fig. 2 (from Ref. 13).

**Fig. 2 Molecular nanostructures by *self-assembly*.**



In turn, phase changes in evolving nanocolloids may notably affect macroscopic properties of the bulk nanofluid. In petroleum, the majority of self-assembling molecules belong to the solubility-defined fraction of “asphaltenes”.<sup>14-17</sup>

### **Colloidal Suspensions and Association Nanocolloids in Petroleum**

Specialists in the subject may argue that there is no novelty in importance for petroleum properties of native colloids (either micrometer- or nanometer-sized). Indeed, this importance has been emphasized several decades ago, firstly with respect to bitumen.<sup>18,19</sup> Later, it was recognized that any petroleum medium represents a colloid system with dispersed colloidal phase constituted predominantly of asphaltenes. The details of asphaltene colloid characterization have been reported in numerous references. The important milestones in this research were publications of a book based on materials of 1993 International Symposium on the Characterization of Petroleum Colloids<sup>20</sup> and of a Russian-language book on disperse systems in petroleum.<sup>21</sup>

However, neither earlier, nor more recent models of asphaltene colloids in petroleum include a concept of asphaltene self-assembly into a variety of (nano)colloidal configurations with a well-structured phase diagram.

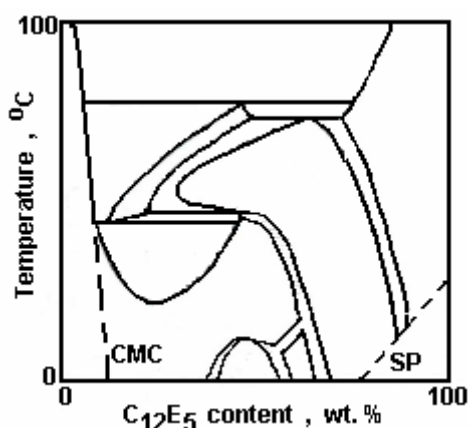
In most models (cf. Ref. 22 and multiple references therein), asphaltenes from the start are regarded as *solid* (quasispherical) colloidal particles with diameters of 2-10 nm. Under evolving conditions these colloids may coagulate/flocculate via diffusion-

or reaction-limited processes into larger and larger aggregates until these loose buoyancy and precipitate out of the liquid. Evidently, in these essentially continuous schemes there are no complex phase diagrams of hard sphere colloids, the only “critical boundary” being not a specific phase transformation, but a precipitation onset.

Just one additional “critical boundary” appears in colloidal models where colloidal particles are not permanently present in petroleum but are formed from molecular solutions of asphaltenes at certain critical conditions as a result of some association processes which, for a long period of time, were regarded to be similar to micellization phenomena of simple surfactants. “Critical micellization concentration” (“CMC”) of asphaltenes has been the subject of numerous publications,<sup>23</sup> though now it is realized that some processes other than text-book “micellization” should be responsible for this particular structural transformation of asphaltene (nano)colloids.<sup>24</sup>

Apparently, it never has been realized that the assumption of “micellization” places asphaltenes into a principally different class of disperse systems. A system of solid particles dispersed in a liquid is classified as a “colloidal suspension”,<sup>25</sup> while systems with particles which are formed by reversible “micellization” are classified as “association colloids”<sup>25</sup> which usually exhibit a very rich phase behavior ranging from the simplest isotropic micellar phases to highly organized supramolecular nanostructures.<sup>26</sup>

**Fig. 3. A complex T-C phase diagram for association colloids in a binary surfactant/water system. Dashed critical boundaries are those for conventional “micellization” (CMC) and for solid precipitation (SP) (adapted from Refs. 26,27).**



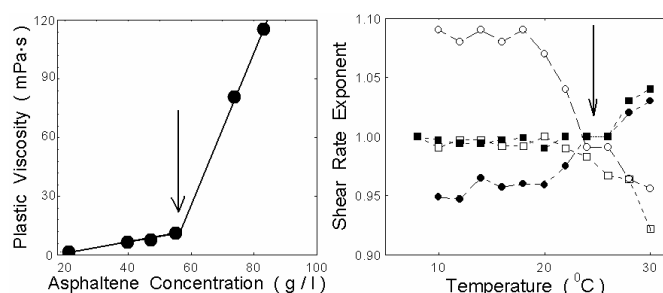
As an example, Fig. 3 shows a complex temperature-concentration (T-C) phase diagram for nonionic surfactant penta-ethyleneglycol dodecyl ether ( $C_{12}E_5$ ) in water.<sup>27</sup> Note the appearance of enclosed phase domains (“closed loops”) at the phase diagram, representative of a so-called reentrant phase behaviour.<sup>28</sup> For further discussion it is important that “closed loops” are indicative of polymorphism of a system;<sup>29</sup> these loops originate in liquid-liquid immiscibility phenomena and are characteristic signatures of directional noncovalent (e.g. hydrogen) bonding in associating species.<sup>30</sup>

It is amazing that after introducing a concept of “micellization” for nanoparticles of asphaltenes, the petroleum researchers remained content with the obsolete notion of a single critical concentration (CMC) in surfactants. Consequently, a possible analogy with known complex properties of association colloids (rich phase diagram, hence multiple critical concentrations/temperatures) has not been investigated, though, as shown in the following sections, well-known published experimental results and recent publications provide multiple data in support of the concept of asphaltenes being “*association nanocolloids*”.

### T-C Phase Diagram of Asphaltenes in Petroleum – Data Accumulation

Phase changes in asphaltene-containing systems can be identified by revealing “specific points” (singled out by step-like changes, extrema, inflections etc.) in experimental concentration and temperature dependencies of system’s parameters. Fig. 4 shows an example from our publication on concentration and temperature effects on Herschel–Bulkley’s rheological parameters in asphaltene-rich model oils.<sup>31</sup>

**Fig. 4. Identification of specific/critical points for asphaltene phase diagram in experimental data sets (adapted from Ref. 31).**



In the absence of artifacts, the above “specific points” may be expected to form well-defined phase boundaries on a T-C graph. The T-C area of possible practical importance is wide: from pour point temperatures to those of asphaltene decomposition/coking and from “infinitely diluted petroleum solutions” to solid asphaltenes. Over the past decades, a number of experimental groups have published a large volume of experimental data, which show a presence of “specific points” in various parts of the above T-C area for asphaltenes. E. g., our research group investigated *concentration* effects in dilute solutions with asphaltene contents from ~1 mg/l to ~1 g/l, mostly close to room temperatures.<sup>32-34</sup> On the other hand, detailed studies of *temperature* effects in the range from -50°C to ~400°C have been performed<sup>35-37</sup> with bitumen and precipitated asphaltenes, i.e. for asphaltene concentrations from ~140 g/l to ~1200 g/l.

Some specific concentrations/temperatures were neither noticed, nor discussed in original publications, but the corresponding “specific points” are clearly seen in the published data plots. E. g., SANS study of asphaltene aggregation<sup>38</sup> provided detailed concentration dependencies of the radii of gyration  $R_G$  in solutions of asphaltenes with concentrations 3.4 - 117 mg/l, at temperatures from 8°C to 73°C. The authors made a qualitative discussion of concentration/temperature effects, but did not specify obvious  $R_G$  maxima at concentrations ~5, ~20-22 and ~70 g/l. Moreover, their original data, being re-plotted on  $R_G$  vs T graph clearly indicate the presence of “specific temperatures” of about 28-32°C.

In a single journal paper it is impossible to make a complete list of all relevant references; other sources of “specific points” used for constructing the T-C phase diagram will be listed in a forthcoming publication.

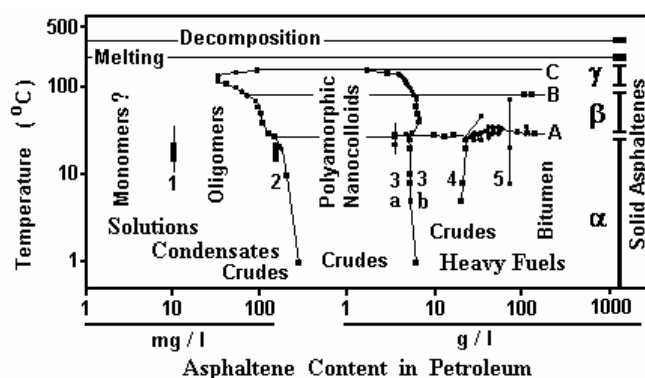
### **T-C Phase Diagram of Asphaltenes in Petroleum – Current Version**

To our knowledge, there have been no attempts to make a comparative analysis of all available information on “specific points” in asphaltene-containing media. In Fig. 5 we present a first cumulative T-C plot of all “specific points” obtained as described in the previous section. As can be seen from the figure, currently available experimental evidence already is sufficient for revealing some fairly well-defined phase boundaries in the T-C phase diagram. However, the still limited amount of data does not allow any statistical analysis; hence all below



discussed numerical values of “critical” parameters should be regarded as approximate and will be subjected to further investigation.

**Fig. 5. A complex T-C phase diagram for association nanocolloids of asphaltenes in petroleum media, constructed on the basis of the (limited) currently available data.**



### Concentration-Defined Phase Boundaries

**Primary aggregation boundary** (line 1 in Fig. 5). The first experimental evidence for this primary aggregation stage at ca. 7-10 mg/l (at 20°C) was obtained by measuring UV/vis absorption, viscosity and NMR relaxation in toluene solutions of solid asphaltenes and of heavy crude oils<sup>32-34</sup>. Attribution of this boundary to primary association of asphaltenes monomers recently was also confirmed by fluorescence technique.<sup>39</sup>

**Liquid-liquid demixing boundary** (line 2 in Fig. 5). This boundary (ca. 100-150 mg/l at 20°C) has been revealed for solutions of solid asphaltenes and of heavy crudes by measurements of optical absorption,<sup>32-34</sup> of NMR relaxation,<sup>33,34</sup> of viscosity,<sup>33,34,40</sup> of ultrasonic velocity,<sup>41</sup> etc. A well-known feature of demixing systems is a closed-loop phase boundary at T-C diagram.<sup>28-30</sup> An inspection of Fig. 5 shows that, indeed, phase boundaries 2 and 3 tend to be parts of such loop. Other characteristic boundaries of closed-loop T-C diagrams are “upper” and “lower” “critical solution temperatures” (UCST and LCST) which, apparently, also are present in Fig. 5.

**“Former CMC” boundaries** (lines 3a and 3b in Fig. 5). “Specific points” at ~1-10 g/l are the most documented one, owing to a large magnitude of abrupt changes in concentration dependencies virtually of all measurable parameters.<sup>42</sup> More detailed inspection shows that published “CMC” data tend to concentrate at two sub-ranges,

namely at  $\sim 1\text{-}3$  g/l and at  $\sim 7\text{-}10$  g/l. As discussed above, for many years, these specific points have been interpreted by employing the concept of CMC, projected from surfactant science. When it became clear that asphaltenes do not exhibit true CMC behavior, a new abbreviation was introduced - CNAC (critical nanoaggregate concentration).<sup>43</sup> Fig. 5 shows that the “former CMC” boundaries reflect phase transformations not in primary systems of asphaltene molecules, but in secondary systems of complex nanocolloids formed at the demixing boundary. Moreover, as indicated above, at least one of “former CMC” lines may appear to be just a continuation of a demixing (liquid-liquid separation) closed loop.

**Highest-concentration boundaries** (lines 4 and 5 in Fig. 5). In studies of “CMC” by viscosity measurements<sup>44</sup> additional strong effects were observed at  $\sim 20\text{-}35$  g/l (line 4 in Fig. 5) and were ascribed to a “second aggregation concentration”. As a result of detailed SANS studies, phase behavior in the highest-concentration range was interpreted as follows.<sup>38</sup> In the “dilute regime” (between boundaries 3 and 4 in Fig. 5) asphaltene aggregates are independent entities with radii of a few nanometers. In the “semidilute regime” (above boundary 4 in Fig. 5) the internal structure of aggregates remains unchanged, but these aggregates interpenetrate and form soft fractal objects, imparting high fluid viscosities. The “concentrated regime”, apparently above  $\sim 70\text{-}90$  g/l (boundary 5 in Fig. 5), is characterized by the appearance of a phase consisting of large ( $>0.1$   $\mu\text{m}$ ) flocculated asphaltene domains, which may form “spatially-organized two-phase textures” (gel-like structures) and sedimentation of this phase may also occur. Hence, in simpler fluids, boundary 5 may be regarded as a “free-flowing” limit. Higher asphaltene concentrations apparently are encountered only in multicomponent highly viscous/gelled systems (bitumen).

### **Temperature-Defined Phase Boundaries**

The majority of experimental data on “specific temperatures” has been obtained for asphaltene-rich bitumen and for corresponding neat (solid) asphaltene fractions.<sup>35,45-47</sup> In short, these experiments revealed the presence of several temperature-controlled phases of aggregated asphaltenes (cf. the right-hand part of Fig. 5). At freezing temperatures (not shown in Fig. 5) asphaltenes exhibit a heat capacity consistent with that of an ordered solid, while at ca.  $-30^\circ\text{C}$  they undergo a phase transition to an amorphous (glassy) phase, structurally controlled by interactions between polar

alkane side chains, and dominant up to 25-30°C (denoted as  $\alpha$ -phase in Fig. 5). In a following phase transition asphaltenes acquire more dense structures, which are fairly stable up to ca. 100°C, and are controlled by bonding to pericondensed aromatic segments, ( $\beta$  phase in Fig. 5). In 100-180°C temperature range there appear yet another asphaltene phase with some crystalline order ( $\gamma$ -phase in Fig. 5). At higher temperatures, amorphous asphaltenes soften and liquefy, while crystalline domains melt at ~220-240°C. Finally, above ca. 350°C, asphaltenes decompose and form liquid crystalline mesophase, precursor of coke.

For asphaltene-containing free-flowing fluids, including native crudes, the best documented specific temperatures fall onto **the  $\alpha$ - $\beta$  phase boundary** in the range of 25-35°C (line A in Fig. 5). E. g., a transition to a more dense ( $\beta$ ) phase was manifested by noticeable shrinking of complex asphaltene aggregates,<sup>38</sup> by a decrease of surface tension<sup>44</sup> and by an increase of deposition from asphaltene solutions.<sup>14</sup> In support of the above discussed demixing phenomena, this boundary has been interpreted as “upper critical solution temperature” (UCST) both in bitumen<sup>45</sup> and in asphaltene solutions.<sup>48</sup> Comparatively less investigated are the  **$\beta$ - $\gamma$  phase boundary** (line B in Fig. 5) and the **upper  $\gamma$ -phase boundary** (line C in Fig. 5). At the “closed loop” domain the latter boundary may be identified with “lower critical solution temperature” (LCST).

The data of Fig. 5 show that temperature-driven transitions between  $\alpha$ ,  $\beta$  and  $\gamma$  phases are observed at all asphaltene concentrations above the demixing boundary (line 2). Hence, apparently, these phases are inherent already to the primary asphaltene nanoparticles and, most probably, their inner structures are controlled by different types of possible bonding of asphaltene monomers, as discussed above. In view of thermally-induced variations of structural order, earlier proposed models of primary aggregates may be more closely related, than conventionally believed. Among these models are “asphaltene crystallite” with some degree of order,<sup>49</sup> more disordered “hairy tennis ball”<sup>50</sup> and “polymer structure”<sup>51</sup>, a liquid-like “glassy droplet”.<sup>52</sup>

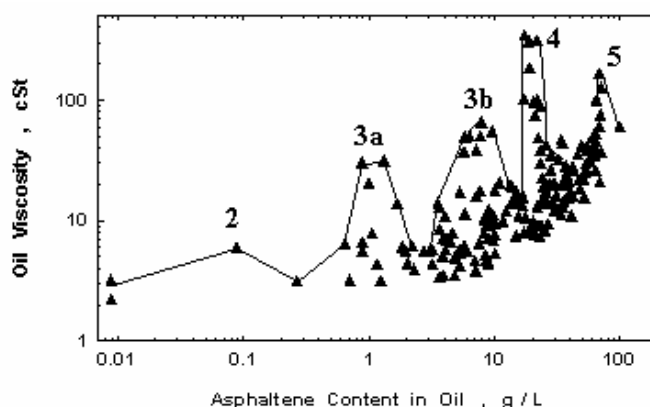
### **Immediate Relevance to the Properties of Native Petroleum**

We are aware that some skeptical reservoir engineers may wonder: “who needs these scientific speculations and nice pictures obtained in laboratory exercises

with artificially designed formulations; most probably all this is just one more showoff in the fashionable subject of “NANO” with little relevance to honest reservoir fluids?” It is true that at the moment we can not make any suggestion about the details of nanocolloid phases in “live” petroleum - this will need much more complicated and costly experiments. However, a detailed inspection of available information on the properties of world’s “dead” (recovered) petroleum fluids show surprisingly strong effects which may originate in the phase diagram of asphaltene nanocolloids of Fig. 5. In particular, we have compiled a database for several hundreds of recovered world’s crudes with various asphaltene contents. Previously published analysis of this database<sup>53</sup> did not take into account the newly obtained information on asphaltene phase diagram, which now highlights some of the previously overlooked features.

As an example, Fig.6 shows a log-log plot of viscosity vs asphaltene content for ca. 200 crudes of various geographical/geological origin. The solid line in Fig. 6 has no special significance and is drawn just to emphasize the apparent viscosity extrema.

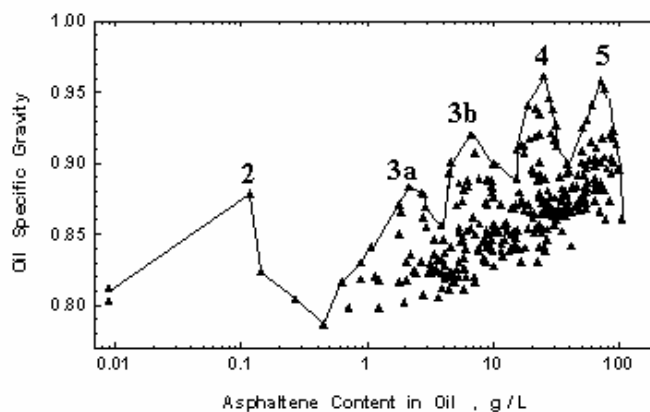
**Fig. 6. Complex variations of viscosity with asphaltene content for world’s (dead) crudes. Apparent extrema are numbered in accordance with asphaltene phase boundaries in Fig. 5.**



For quantitative interpretation of underlying mechanisms, the statistics has to be improved, especially in the range of low asphaltene contents; nevertheless even the “raw” data of Fig. 6 clearly demonstrate a striking coincidence of sharp viscosity anomalies with **all** (but one) phase boundaries of asphaltene nanocolloids in Fig. 5. Phase boundary 1 corresponds to oil’s asphaltene content of ca. 0.001 wt% while most current databases classify all values below 0.01 wt% as “zero asphaltene content”.

Note that Fig. 6 shows a virtual absence of native free-flowing crude oils with asphaltene contents above the phase boundary 5 which, as discussed above, may be a natural “solubility limit” of asphaltenes in native crudes.

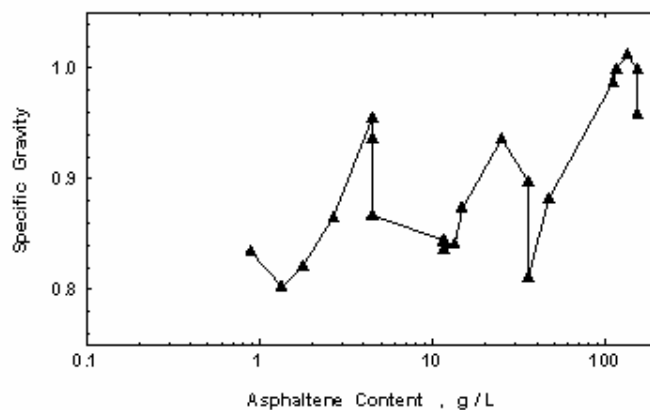
**Fig. 7. Complex variations of specific gravity with asphaltene content for world’s (dead) crudes. Apparent extrema are numbered in accordance with asphaltene phase boundaries in Fig. 5.**



There is a well-known interdependence of viscosities and of specific gravities (densities) in crude oils. Indeed, our database reveals noticeable peaking of specific gravities at asphaltene phase boundaries, as shown in Fig. 7.

In fact, “asphaltene nanophase” effects are so persistent, that once one starts searching for them, they emerge even in very limited data collections. E. g., a Web site on asphaltene deposition presents a table with “Resin and Asphaltene Content of various Crude Oils”.<sup>54</sup> The table contains properties of just ca. 20 crudes with non-zero asphaltene content from diverse locations (Canada, Venezuela, Mexico, USA, Russia, Brazil, Iraq, France, Algeria). A plot of specific gravity vs. asphaltene content for this collection of oils is shown in Fig. 8. In the absence of the above discussed data, the peculiar behavior of data points would be regarded merely as an extensive scatter. However, comparison with the larger database of Figs. 6 and 7 allows attributing peaks of specific gravity to the same asphaltene phase boundaries (boundary 3b is not reproduced due to the lack of data points in the respective concentration range).

**Fig. 8. Complex variations of specific gravity with asphaltene content in the limited collection of world's (dead) crudes.**



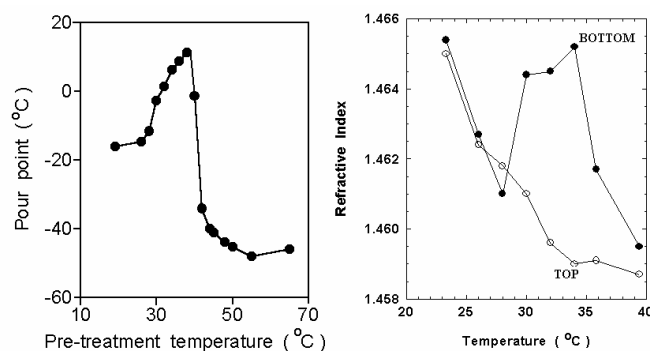
Our experiments revealed noticeable transformations of the macroscopic properties of native crudes at the temperature-defined nanophase boundary “A” in Fig. 5.

The left-hand part of Fig. 9 shows variations of the pour point of a Tatarstan crude after 1 hour thermal pre-treatments at temperatures close to the discussed phase boundary.<sup>55</sup> The crude had a density of 895 g/l, contained ~3.5 wt. % asphaltenes, ~20 wt. % resins, ~0.3 wt. % waxes. First deviations of the pour point became noticeable after pre-treatment at ca. 30°C, while the most dramatic increase, from -16.2 to +11.2 °C, was registered after pre-treatment at temperature of 37.5 °C.

The right-hand part of Fig. 9 shows dramatic density stratification near the discussed asphaltene nanophase boundary “A” in 10 cm-high samples of a Yamal native crude (West Siberia), stored at various temperatures. Density variations were evaluated via refractive index (RI) measurements in the minute quantities of oil extracted from the top and from the bottom of the sample. In the absence of “phase boundary” phenomena, an expected effect is a gradual decrease of RI due to thermal expansion, with the density at the top being only marginally smaller than at the bottom. Indeed this behavior was observed below ca. 28 °C and, once again, above ca. 37 °C. At intermediate temperatures, in the vicinity of asphaltene nanophase boundary, there was a strong transient stratification of density and, presumably of composition of the oil.

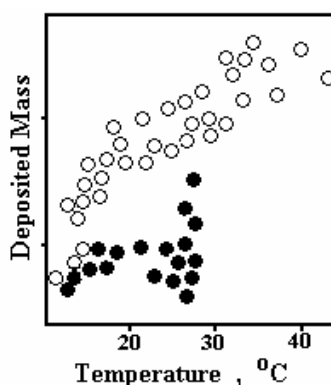
Some of the effects induced at the nanophase boundary “A” may be very long-lived, apparently governed not by thermodynamic but by kinetic control.<sup>14</sup> E.g., pour point changes, illustrated in Fig. 9, persisted for as long as four months.<sup>55</sup>

**Fig. 9. Strong variation of native crude oil properties at asphaltene nanophase boundary “A” in Fig. 5.**



Another example of long-lived effects is from our recent study of deposits at steel surfaces from petroleum fluids with high asphaltene content (12.3 g/l).<sup>14</sup> Filled symbols in Fig. 10 show deposits from a fluid which in its “thermal history” never has crossed the phase boundary “A”. Open symbols show deposits from a fluid at least once heated above 28-29°C. After that, the increase of deposition, characteristic to higher-temperature nanophase, persisted below the phase boundary (at 12-29°C) for at least one month.

**Fig. 10. Kinetically controlled long-lived increase in the mass of deposits from petroleum media, induced at asphaltene nanophase boundary “A” (adapted from Ref. 14).**

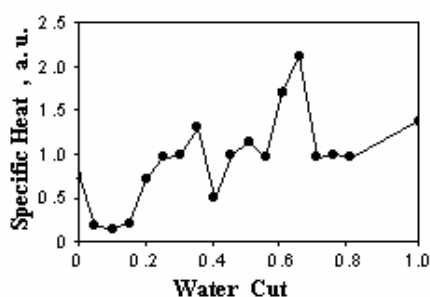


## Nanophase-Resembling Phenomena in Brine- Petroleum Dispersions

The output of a production oil well consists typically of a dispersion of formation water (brine) in a crude oil. Detailed knowledge of the properties of these dispersions is necessary if the behavior and characteristics of multiphase flows are to be predicted correctly.<sup>56</sup> Certainly, reservoir water/oil mixtures are not “nanosystems”. However it appears that from the practical point of view, their properties may resemble those of the above discussed nanocolloids in a sense that morphological behavior of water-in-oil dispersions is characterized by well-structured “phase diagrams”. Moreover, w/o dispersion morphology is known to be controlled by oil’s “indigenous surfactants” including nanocolloidal asphaltenes.<sup>57</sup>

As an example, Fig.11 shows complex variations of an effective specific heat of freshly prepared w/o emulsions at 20-25 °C, subjected to microwave heating. The native crude oil was collected a well-head at Korobkovskoye reservoir (Russia), had a density of 832 g/L, contained ca. 1 wt. % asphaltenes, 8 wt. % resins, 2 wt. % waxes; the water was a double distillate with pH≈5.5. Sharp variations of specific heat were attributed to abrupt changes of dispersion’s morphology/phase state, strongly resembling those observed in model nanoemulsion/microemulsion systems.<sup>58</sup> In particular, “percolation threshold” obviously occurs at water cuts close to 0.2, phenomena at water cuts close to 0.4 most probable are due to emergence of “bicontinuous morphology” while “close packed” phases emerge at water cuts above 0.6.

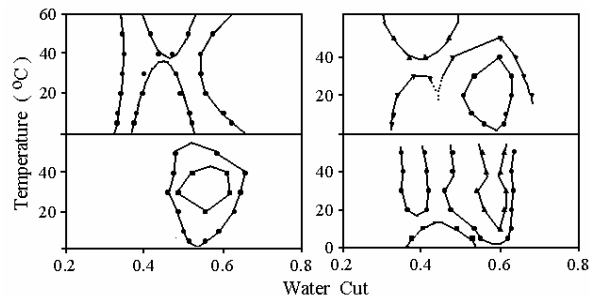
**Fig. 11. Specific heat variations due to “nano-resembling” changes in phase morphology of native w/o dispersions.**





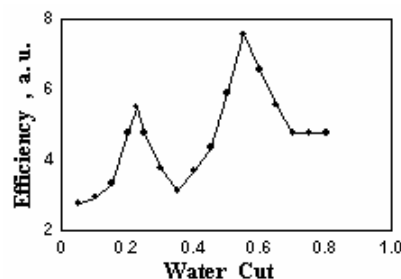
A complex “*nano-resembling*” phase behavior may be a fairly common property of native brine/oil emulsions, as indicated by our density measurements for mixtures of 12 native (dead) crude oils with their respective oilfield brines.<sup>59</sup> Easily detectable nonzero excess (non-ideal) densities for water cuts from 0.4 to 0.6 were regarded as indicative of formation of a dense asphaltene-mediated “middle phase” with an apparent bicontinuous morphology. Fig. 12 shows T-C contours of equal excess (non-ideal) density for four representative w/o dispersions. The shapes of excess density “phase domains” strongly resemble bicontinuous domains of T-C phase diagram for association nanocolloids in Fig. 3.

**Fig. 12. The complex morphology/phase behavior of native brine/oil dispersions, as revealed by density measurements. (Adapted from Ref. 59).**



Of an immediate practical importance is a substantial increase of demulsification efficiency (inverse time of the onset of free phase separation) in w/o emulsions with “*nano-resembling*” morphologies. Fig. 13 shows improved microwave demulsification at specific water cuts attributed to “percolation” and “bicontinuous” phenomena (cf. Fig. 10).

**Fig. 13. Efficiency of microwave demulsification of water emulsions in a native crude oil.**



## **What May be Regarded as a Petroleum-Oriented Nanotechnology for Reservoir Engineering?**

Our opinion is that the term “nanotechnology” may be used for any industrial operations which are designed and performed with an understanding of importance of the above discussed complex nanophase diagrams of petroleum fluids. Such technology should include specifically designed processes (employ specifically selected parameters) to purposely avoid/instigate particular phase transformations in petroleum nanocolloids in order to improve (or, at least, not to ruin) the practically important bulk properties of petroleum.

E. g., any lengthy operations in the vicinity of the temperature-defined phase boundary “A” (cf. Fig. 5) should be avoided in view of undesirable increase of viscosity and pour point (cf. Fig. 9), as well as of deposition (cf. Fig. 10) at lower temperatures. On the other hand, intentional storage of petroleum at this phase boundary may be employed to facilitate increased stratification of petroleum light/heavy components (cf. Fig. 9). Hypothetically, mechanical removal of some strata may constitute a low-cost method of improving oil quality.

Approaching a concentration-defined nanophase boundary by blending of crude oils may be the cause of some severe compatibility problems like noticeable viscosity and density peaking (cf. Figs. 6, 7). Alternatively, blending of viscous/dense crudes with native asphaltenes at critical concentration boundaries (e.g. ca. 8 and ca. 20 wt. %) will provide a product (containing ca. 14 wt. % asphaltenes) with greatly improved properties as follows from the data of Fig. 6 and of Fig. 7.

With respect to immediate practical applications, it should be emphasized once more that the above discussed T-C diagrams contain only “the most obvious” nanophase boundaries, reflect our *current knowledge* of structural transformations in petroleum and should be subjected to further investigation.

## **Conclusions**

At present, practical/commercial examples of “nanotechnology” are almost exclusively from such industrial domains as electronic microchip fabrication, construction of new materials, pharmacology/cosmetics and biomedical sciences. In petroleum industry, “nanotechnologies” still are not considered to be important enough for widespread practical applications, with only exception being refinery

processes. In upstream applications, most attention is currently devoted to research in development of new nanostructured “smart fluids” for EOR/IOR and drilling operations.

However, our research shows that now there is enough factual evidence to consider native crude oils themselves as “association nanofluids”. Hence, we suggest that conventional/emerging technologies for reservoir engineering should become “nanotechnologies” in a sense that they should be optimized/designed with an account for (still under-investigated) complex phase diagrams of intrinsic petroleum nanocolloids, primarily those formed by asphaltenes. At the least, this would help to preserve a delicate inner structure of native crudes (the approach which may be regarded as “petroleum nanoecology”).

Moreover, it appears that such optimization may be required also with respect to handling some macroscopic disperse systems like reservoir water / crude oil dispersions which are “nano-resembling” in a sense that their behavior may be characterized by well-structured morphological/phase diagrams.

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